

PHYS 324 – Thermodynamics
Spring 2008

Homework 6: (due Feb 27th)

1. Pure plutonium forms six different equilibrium solids at atmospheric pressure. What this means is that Pu can have six different crystal structures, and therefore there are six phases of solid Pu. The transformation enthalpies are as follows:

Transition (phase 1 → phase 2)	$\Delta\bar{H} \left[\frac{K \cdot Cal}{mol} \right]$	$T_{eq}^{trans} [K]$
$\alpha \rightarrow \beta$	0.8	395
$\beta \rightarrow \gamma$	0.15	478
$\gamma \rightarrow \delta$	0.13	591
$\delta \rightarrow \epsilon$	0.02	724
$\epsilon \rightarrow \text{liquid}$	0.44	749

The standard enthalpy of formation (i.e., the zero of the enthalpy scale of Pu at STP) is $\bar{H}(T = 298 K, P = 1 atm) = 0$ and the entropy at STP is $\bar{S}(T = 298 K, P = 1 atm) = 13.2 \text{ cal/(K mol)}$.

The molar heat capacities are given in the following table (note that for the first three phases the heat capacities are weak functions of temperature):

phase of Pu	$\bar{C}_P \left[\frac{cal}{K \cdot mol} \right]$	temperature range [K]
α	$5.91 + 5.8 \times 10^{-3} T$	298-395
β	$5.21 + 7.05 \times 10^{-3} T$	395-478
γ	$2.98 + 11.1 \times 10^{-3} T$	478-591
δ	9.0	591-724
ϵ	8.4	724-749
liquid	8	$749 - T_{boil}$

- a. Calculate the molar enthalpy of Pu and plot it as a function of temperature from $T = 298 \text{ K}$ to $T = 1000 \text{ K}$.

- b. Calculate the molar entropy of Pu and plot it as a function of temperature from $T = 298 \text{ K}$ to $T = 1000 \text{ K}$.
- c. Calculate the molar Gibbs free energy of Pu and plot it as a function of temperature from $T = 298 \text{ K}$ to $T = 1000 \text{ K}$.
- d. Suppose α -Pu at 273 K is mixed with liquid Pu at 1000 K in the ratio of 2:1. What would be the resulting equilibrium phase?

[Hint: This also may be easier done with a computer algebra system such as Maple or Maxima. You need to evaluate the enthalpy, entropy and Gibbs for each temp. range.]

5% extra credit: Find the crystal structures for each stable phase.

2. Carbon has two solid phases: pure graphite and pure diamond. Consider the phase transformation of pure carbon graphite to pure carbon diamond at atmospheric pressure and at temperatures between 298 and 1200 K using the following data:

graphite	$\bar{H}(T = 298 \text{ K}, P = 1 \text{ atm}) = 0$
	$\bar{S}(T = 298 \text{ K}, P = 1 \text{ atm}) = 5.694 \frac{\text{J}}{\text{mol} \cdot \text{K}}$
	$\bar{C}_P(T = 298 \text{ K}, P = 1 \text{ atm}) = 17.2 + 4.27T - \frac{8.79 \times 10^{-5}}{T^2} \frac{\text{J}}{\text{mol} \cdot \text{K}}$
diamond	$\bar{H}(T = 298 \text{ K}, P = 1 \text{ atm}) = 1900 \frac{\text{J}}{\text{mol}}$
	$\bar{S}(T = 298 \text{ K}, P = 1 \text{ atm}) = 2.44 \frac{\text{J}}{\text{mol} \cdot \text{K}}$
	$\bar{C}_P(T = 298 \text{ K}, P = 1 \text{ atm}) = 9.12 + 13.2T - \frac{6.19 \times 10^{-5}}{T^2} \frac{\text{J}}{\text{mol} \cdot \text{K}}$

- a. Plot the change in molar enthalpy for graphite transforming to diamond at 1 atm pressure for temperatures between 298 and 1200 K.
- b. Plot the change in molar Gibbs free energy for graphite transforming to diamond at 1 atm pressure for temperatures between 298 and 1200 K.
- c. Plot each of the molar free energies for diamond and for graphite as a function of the entropy of the system at 1 atm pressure for temperatures between 298 and 1200 K.